

N₈: A Structure Analogous to Pentalene, and Other High Energy Density Minima

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Received: September 7, 1994[⊗]

Ab initio molecular electronic structure methods have been used to examine three isomers of N₈. In addition to the previously studied octaazacubane structure (**1**), we have investigated a *D*_{2d} structure (**2**) analogous to cyclooctatetraene, and a planar bicyclic form (**3**) analogous to pentalene. Using a double- ζ plus polarization (DZP) basis set, we have optimized geometries with the Hartree–Fock self-consistent-field (SCF) method, with second-order Møller–Plesset perturbation theory (MP2), and with single and double excitation configuration interaction (CISD) and coupled-cluster (CCSD) methods. Harmonic vibrational frequencies and infrared intensities have been obtained at the SCF and MP2 levels of theory. Although cubane and cyclooctatetraene are known experimentally, unsubstituted pentalene has never been synthesized; nevertheless, our vibrational analysis indicates that *all three* nitrogen analogues, including the pentalene analogue **3**, represent potential energy minima. The metastability of **3** is attributed to two additional π electrons present in **3** but not in pentalene, according to the rule of topological charge stabilization. Further, since all three minima are very high-lying with respect to 4N₂, we have examined their potential application as high energy density materials (HEDMs). Our highest-quality results place the pentalene-like structure **3** approximately 225 kcal/mol above 4N₂, 198 kcal/mol below **1**, and 35 kcal/mol below **2**.

Introduction

The development of efficient and safe conventional propellants and fuels is a goal of obvious technological significance. A high ratio of energy release to mass is clearly a desirable quality of such a propellant. Several theoretical studies to identify such high-energy density material (HEDM) candidates have been carried out over the last several years in our laboratory. Our theoretical studies to date have shown that the cyclic O_{*n*} systems (*n* > 5) are potential high energy density materials;^{1–4} they are particularly appealing in that, under complete combustion with molecular hydrogen, they release water as the only new molecular product.

Other candidates for environmentally safe HEDMs are the N_{*n*} molecules. Bliznyuk et al. have shown that N₂₀ has a metastable dodecahedral geometry, as one might expect by analogy to C₂₀H₂₀ dodecahedrane.⁵ Lying approximately 50 kcal/mol of nitrogen atoms above 10N₂, the N₂₀ molecule might make a very effective high energy density material if it could be synthesized. Here we use ab initio electronic structure methods to determine the energies and stabilities of three N₈ structures. The first of these, octaazacubane (**1**), has already attracted theoretical interest. Using a pseudopotential SCF method, Trinquier et al.⁶ were the first to report theoretical results for **1**. They found that **1** is even higher in energy than 2N₄, which is very high-lying. These workers assumed that their optimized N₈ stationary point was a minimum on the potential energy hypersurface.

Engelke and Stine⁷ showed that **1** is indeed a minimum at the SCF level by performing vibrational frequency calculations using STO-3G, 4-31G, and 4-31G* basis sets. In addition, these authors showed that N₈ is very energetic at correlated levels of theory, and their estimates of detonation pressure and velocity compared favorably to those of known explosives. Engelke and Stine estimated the activation barrier for the symmetry-forbidden

concerted reaction N₈ → 4 N₂ to be ~160 kcal/mol at the 4-31G* SCF level. If the decomposition were to take place as four [2+2] symmetry-forbidden steps instead, they estimated a barrier of ~40 kcal/mol for each step. Such barriers suggested that **1** might be synthesizable despite its very high energy. Octaazacubane (**1**) has also been examined as part of the series (CH)_{8–*n*}N_{*n*}, where 0 ≤ *n* ≤ 8.^{8,9} These studies indicated that the heat of formation of these compounds increases with increasing *n* and that the high-energy content of the polyazacubanes is due not to strain energy (which is very large in cubane) but to weak N–N single bonds.

Lauderdale et al. were the first to optimize **1** at correlated levels of theory.¹⁰ Their second-order perturbation theory results indicated that correlation has large effects on the equilibrium geometry and vibrational frequencies of **1**. In addition, these workers obtained much more reliable estimates of the energy difference Δ*E*(N₈ – 4N₂) by employing the coupled-cluster singles and doubles method (CCSD).¹¹ Their results confirmed previous conclusions that **1** is a high-energy metastable species.

In this study, we extend the theoretical consideration of the N₈ potential energy hypersurface to two previously uninvestigated isomers: an all-nitrogen analogue of cyclooctatetraene (**2**) and a planar bicyclic structure of *D*_{2h} symmetry (**3**), analogous to pentalene. Using a DZP basis set, we report optimized geometries and harmonic vibrational frequencies for **1**, **2**, and **3** at correlated levels of theory. Although unsubstituted pentalene has never been prepared, we find the all-nitrogen analogue **3** to be a minimum on the potential energy surface at the levels of theory (DZP SCF and DZP MP2) investigated. Structures **1** and **2** also represent minima at these levels of theory. High-quality estimates of the energy differences between the three N₈ structures and 4N₂ are determined using the CCSD(T) method.¹² Finally, we consider each structure as a high energy density material candidate.

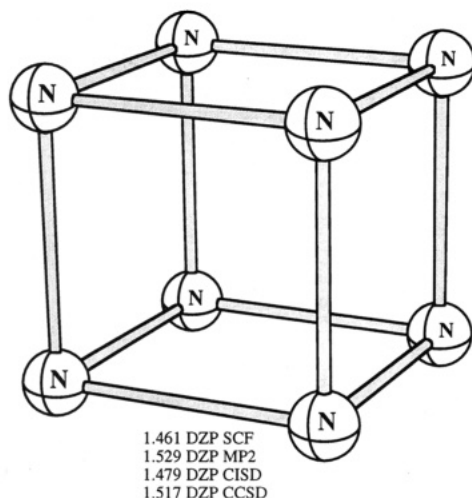
Theoretical Approach

The double- ζ plus polarization (DZP) basis employed in this study is the standard Huzinaga–Dunning^{13,14} double- ζ basis

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[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1995.



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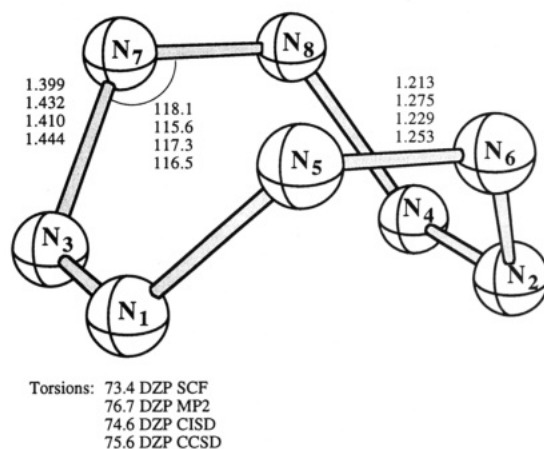
Figure 1. Theoretical equilibrium geometries of the O_h symmetry octahedral structure of N₈. Bond lengths are in angstroms, and bond angles are in degrees.

augmented with a set of six d-like polarization functions on each atom [$\alpha_d(N) = 0.80$]. This basis is described as N(9s5p1d/4s2p1d), and it consists of 128 contracted Gaussian basis functions. The theoretical methods employed are restricted Hartree–Fock (RHF) self-consistent-field (SCF), second-order Møller–Plesset perturbation theory (MP2), and single and double excitation configuration interaction (CISD)¹⁵ and coupled cluster (CCSD).^{11,16} For the CI wave functions, the contribution of unlinked quadruple excitations is estimated by Davidson's formula.¹⁷ For coupled-cluster wave functions, the additional effect of connected triple excitations was estimated perturbatively according to the CCSD(T) method.^{12,18}

Geometries were optimized using analytic first derivatives at the SCF,¹⁹ MP2,²⁰ CISD,²¹ and CCSD²² levels of theory. Harmonic vibrational frequencies were determined via analytic SCF second derivatives^{20,23} or by finite differences of the analytic MP2 first derivatives. Infrared intensities were determined analytically at the SCF level,²⁴ while the MP2 infrared intensities were evaluated via finite differences of dipole moments. For the CI and coupled-cluster methods, the core orbitals (N 1s-like) were constrained to be doubly occupied and the corresponding eight virtual orbitals were deleted from the correlation procedure. The wave functions for octaazacubane (1) and for the boat structure (2) were obtained under C_{2v} symmetry. For the CISD wave functions there were 424 637 configuration state functions (CSFs) for the octaazacubane (1) and boat (2) structures and 221 921 for the D_{2h} bicyclic structure (3). The PSI ab initio programs²⁵ were used in the present study. MP2 results were obtained with the Cambridge Analytic Derivatives Package (CADPAC).²⁶

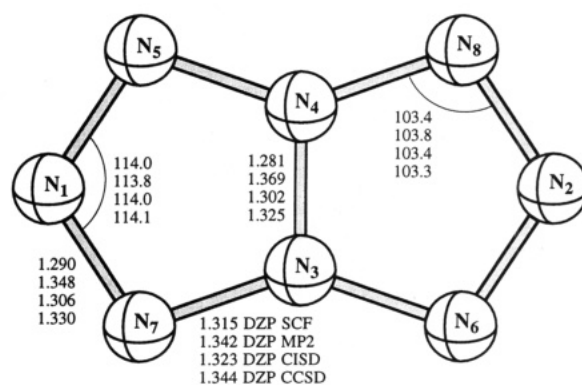
Results and Discussion

The geometric parameters of the three N₈ structures are given in Figures 1–3. Systematic studies have shown that a proper balance between basis set and correlation method must be maintained in order to obtain accurate theoretical geometries. Thomas et al.²⁷ have found that, for small molecules, the DZP SCF method tends to underestimate experimental equilibrium bond lengths, while the DZP CCSD method tends to slightly overestimate them. The method giving the most accurate bond distances in their study is DZP CISD. Because CISD is not size-extensive, its treatment of electron correlation is likely to



(2)

Figure 2. Theoretical equilibrium geometries of the D_{2d} boat structure of N₈. Bond lengths are in angstroms, and bond angles are in degrees.



(3)

Figure 3. Theoretical equilibrium geometries of the D_{2h} planar structure of N₈. Bond lengths are in angstroms and bond angles are in degrees.

be less complete in the present study of N₈ isomers with 56 electrons, leading to relatively shorter theoretical bond lengths. We therefore anticipate that the true equilibrium bond lengths lie somewhere in between those determined at the DZP CISD and DZP CCSD levels of theory.

The N–N bond length in octaazacubane (1) at the SCF level is 1.461 Å, and it increases by 0.068, 0.018, and 0.056 Å using the MP2, CISD, and CCSD methods. The large increases at the CISD and CCSD levels of theory indicate the importance of correlation for this structure. Since we expect the DZP CCSD method to slightly overestimate bond lengths, the even larger bond lengths at the DZP MP2 level demonstrate that DZP MP2 significantly overestimates the effects of correlation on the geometry of 1. The CISD and CCSD bond lengths of 1.479 and 1.517 Å are somewhat longer than a typical N–N single bond (1.449 Å).²⁸ The theoretical geometries for structures 2 and 3 demonstrate the same general trends in the effect of correlation method on equilibrium bond lengths. In most cases, the bond lengths are predicted according to $r_e(\text{SCF}) < r_e(\text{CISD}) < r_e(\text{CCSD}) < r_e(\text{MP2})$, with the CISD and CCSD bond lengths typically 0.01–0.02 and 0.03–0.04 Å, respectively, longer than the SCF values. The CISD and CCSD values for the two unique bond lengths in the boat structure (2) are somewhat larger than typical experimental values for N–N single (1.449 Å) and double (1.252 Å) bonds.²⁸ The bond lengths for the planar structure (3) at correlated levels fall between experimental values for typical N–N single and double bonds, and they are all fairly close to one another. Such bond lengths are what one might

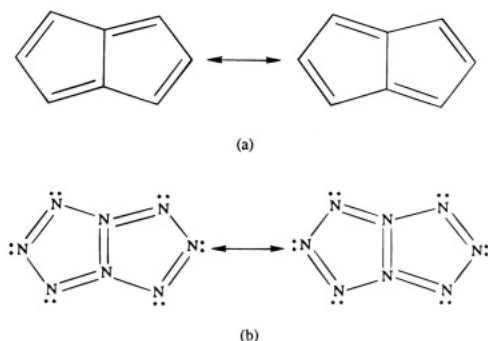


Figure 4. Lewis structures for (a) pentalene and (b) octaazapentalene (3).

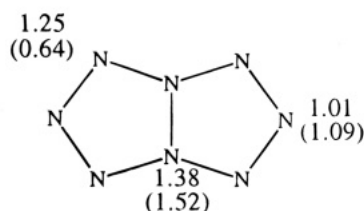


Figure 5. Mulliken charges due to π electrons for octaazapentalene (3) and its dication. Dication charges are in parentheses.

expect for this system: based on the resonance forms of pentalene depicted in Figure 4a, one might guess Lewis structures for **3** as given in Figure 4b (although, admittedly, these Lewis structures have an unfavorable 10 electrons assigned to each of the two bridging nitrogen atoms). The predicted geometries are generally consistent with such Lewis structures.

Although the Lewis structures in Figure 4a suggest resonance stabilization, unsubstituted pentalene has never been prepared. Pentalene dianion, however, is known experimentally.²⁹ One might attempt to explain this difference using the Hückel $4m + 2$ rule for aromaticity, since pentalene dianion has 10 π electrons (a Hückel number) while neutral pentalene has only 8. However, the Hückel rule is justified only for *monocyclic* systems. Gimarc has rationalized the stability difference between pentalene and its dianion using the rule of topological charge stabilization: although the two additional π electrons in pentalene dianion occupy a completely nonbonding molecular orbital, they stabilize the structure by smoothing out the π -electron charge distribution.³⁰ We expect these arguments to remain valid in the case of the all-nitrogen pentalene analogue **3**, so that we attribute the metastability of **3** (vide infra) to the influence of the two extra π electrons which are present in **3** but not in pentalene. In accord with Gimarc's Hückel theory analysis of pentalene dianion, we find that the highest occupied molecular orbital (HOMO) of **3** is a nonbonding π orbital, and that the presence of electrons in this orbital smooths out the π electron charge distribution, as seen by comparing the Mulliken charges due to π electrons for **3** and for its dication (Figure 5). Indeed, at the SCF level the dication of **3** becomes a transition state when optimized under D_{2h} symmetry: the imaginary frequency corresponds to a B_{2g} mode which distorts the molecule into the C_{2h} point group. The C_{2h} minimum of this N_8 dication (Figure 6) represents one of the two localized structures depicted in Figure 4b if one forms the dication by replacing the double bond between the bridging nitrogens in Figure 4b with a single bond. As the quantitative estimation of the equilibrium geometry of the dication of **3** is not important for the current study, we did not pursue optimizations of this structure at correlated levels of theory.

Thus the resonance stabilization suggested by the bond lengths of **3** does not appear to be present for the dication of **3**,

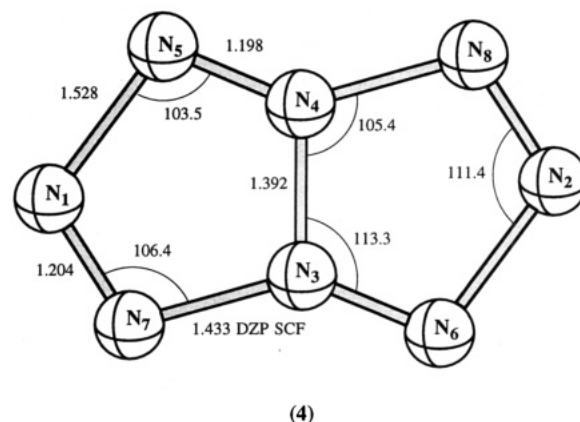


Figure 6. Theoretical equilibrium geometry of the C_{2h} planar structure of N_8^{2+} . Bond lengths are in angstroms and bond angles are in degrees.

TABLE 1: Total Energies (hartrees, Subtract 435) and Energies Relative to $4N_2$ (kcal/mol, in Parentheses) for Various N_8 Stationary Points

level	O_h (1)	D_{2d} (2)	D_{2h} (3)	$4N_2$
DZP SCF	-0.054 757 (490.1)	-0.326 924 (319.4)	-0.398 371 (274.5)	-0.835 856 (0)
DZP MP2	-1.464 236 (449.4)	-1.739 734 (276.5)	-1.827 215 (221.6)	-2.180 432 (0)
DZP CISD	-1.055 002 (450.6)	-1.314 744 (287.7)	-1.391 870 (239.3)	-1.773 154 (0)
DZP CISD+Q ^a	-1.258 123 (440.8)	-1.514 320 (280.1)	-1.586 213 (235.0)	-1.960 642 (0)
DZP CCSD	-1.375 146 (434.4)	-1.632 135 (273.2)	-1.687 547 (238.4)	-2.067 464 (0)
DZP CCSD(T) ^b	-1.439 961 (423.4)	-1.699 530 (260.5)	-1.755 469 (225.4)	-2.114 701 (0)

^a At DZP CISD optimized geometry. ^b At DZP CCSD optimized geometry.

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol, in Parentheses) for O_h Octaazacubane (1)

mode	SCF	mode	MP2
A_{2u}	1356 (0)	A_{2u}	1078 (0)
E_g	1265 (0)	E_g	1016 (0)
T_{2u}	1182 (0)	T_{2u}	893 (0)
A_{1g}	1175 (0)	A_{1g}	886 (0)
T_{2g}	1107 (0)	T_{2g}	808 (0)
T_{1u}	1091 (3)	T_{1u}	748 (7)
T_{2g}	983 (0)	T_{2g}	674 (0)
E_u	735 (0)	E_u	464 (0)

as one might predict by the rule of topological charge stabilization. It would be of interest to apply theoretical tests for aromaticity in hydrocarbons—such as magnetic susceptibility exaltation³¹ or NMR shifts of probe atoms—to this intriguing structure. To our knowledge, this may be the first report of a (meta)stable all-nitrogen aromatic compound (Lauderdale et al. have shown¹⁰ that hexaazabenzene is not a potential energy surface minimum at the DZP MP2 level).

The theoretical harmonic vibrational frequencies and IR intensities for the three structures at the SCF and MP2 levels of theory are given in Tables 2–4. Each structure was determined to be a minimum on the N_8 potential energy surface. Correlation has a large effect on the vibrational frequencies, as evidenced by the 20–37% decrease in the frequencies for octaazacubane (1). These large decreases may be explained in part by the much longer N–N bonds for **1** at the MP2 level. The geometry and frequencies for **1** at the MP2 level are similar to those of Engelke and Stine⁷ and of Lauderdale et al.¹⁰ The MP2 frequencies for the boat structure (2) decrease by 10–

TABLE 3: Harmonic Vibrational Frequencies (cm⁻¹) and IR Intensities (km/mol, in Parentheses) for the N₈ D_{2d} Boat Structure (2)

mode	SCF	mode	MP2
B ₂	1898 (5)	B ₂	1416 (6)
A ₁	1891 (0)	E	1352 (<1)
E	1873 (4)	A ₁	1347 (0)
A ₂	1151 (0)	A ₂	1032 (0)
B ₁	1055 (0)	B ₁	850 (0)
E	960 (1)	A ₁	758 (0)
A ₁	942 (0)	B ₁	713 (0)
B ₁	903 (0)	E	703 (25)
E	839 (9)	E	622 (1)
E	636 (21)	E	540 (13)
B ₂	441 (8)	B ₂	372 (4)
A ₁	381 (0)	A ₁	339 (0)
A ₂	357 (0)	A ₂	294 (0)
B ₁	276 (0)	B ₁	218 (0)

TABLE 4: Harmonic Vibrational Frequencies (cm⁻¹) and IR Intensities (km/mol, in Parentheses) for the N₈ Planar D_{2h} Structure (3)

mode	SCF	mode	MP2
B _{2g}	1663 (0)	B _{3u}	1481 (9)
A _g	1622 (0)	B _{2g}	1391 (0)
B _{1u}	1526 (38)	B _{1u}	1283 (13)
B _{3u}	1484 (11)	A _g	1257 (0)
B _{2g}	1471 (0)	B _{1u}	1206 (49)
A _g	1430 (0)	B _{2g}	1136 (0)
B _{3u}	1300 (26)	A _g	1119 (0)
A _g	1220 (0)	B _{3u}	1106 (<1)
B _{1u}	1154 (153)	B _{3u}	1013 (<1)
B _{3u}	1031 (38)	A _g	962 (0)
B _{2g}	948 (0)	B _{2g}	826 (0)
B _{3g}	818 (0)	A _g	699 (0)
A _g	797 (0)	B _{2u}	665 (<1)
B _{2u}	786 (1)	B _{1g}	656 (0)
B _{1g}	771 (0)	B _{3g}	637 (0)
B _{1u}	545 (2)	B _{1u}	471 (<1)
A _u	420 (0)	A _u	363 (0)
B _{2u}	281 (11)	B _{2u}	234 (8)

29%, while the frequencies of the D_{2h} structure (3) decrease by 7–21% from the SCF results.

At each level of theory the planar bicyclic structure (3) was the most stable, followed by the boat (2) and finally by octaazacubane (1). The energies of each structure at various levels of theory are reported in Table 4, along with the corresponding energies for 4N₂. Each energy is obtained at the equilibrium geometry obtained for that level of theory, except for the CISD+Q and CCSD(T) energies, which are evaluated at the CISD and CCSD geometries, respectively. The equilibrium bond length for N₂ was determined to be 1.083, 1.139, 1.112, and 1.121 Å at the SCF, MP2, CISD, and CCSD levels of theory (experimental *r_e* = 1.098 Å), and the CISD and CISD+Q energies were obtained using a supermolecule approach. The results at correlated levels of theory indicate that the SCF method does not accurately describe the potential energy surface. Since the CISD method is not size-extensive, the CISD relative energies are questionable for a system with as many as 56 electrons. However, with the inclusion of the Davidson correction the energies relative to 4N₂ (tabulated) become comparable to the size-extensive MP2 results. Interestingly, if one uses the CCSD(T) energies as a standard, the MP2 method overestimates the relative energy differences (not tabulated) between 1, 2, and 3, yielding the poorest values for these differences of any of the methods employed, including SCF. Compared to CCSD(T), the MP2 method overestimates the energy differences Δ*E*(2–1) and Δ*E*(3–2) by 10.0 and 19.8 kcal/mol, respectively, while CISD+Q overestimates these differences by 2.2 and 10.0 kcal/mol. At the CCSD(T) level

TABLE 5: Dissociation Energies to O₂/N₂ (kcal/mol of O/N Atoms)

	O ₆	O ₈	O ₁₂	N ₂₀	N ₈ O _h (1)	N ₈ D _{2d} (2)	N ₈ D _{2h} (3)
level of theory	(ref 2)	(ref 3)	(ref 4)	(ref 5)	(this work)	(this work)	(this work)
DZP SCF	22.7	21.6	21.6	51.6	61.3	39.9	34.3
DZP MP2	16.8	15.4		46.2	56.2	34.6	27.7
DZP CCSD(T)					52.9	32.6	28.2
TZ2P SCF	23.3			55.4			
TZ2P MP2	16.5						

TABLE 6: Specific Impulse (*I_{sp}*, seconds) for HEDM Candidates

level of theory	N ₂₀ (ref 5)	N ₈ O _h (1) (this work)	N ₈ D _{2d} (2) (this work)	N ₈ D _{2h} (3) (this work)
DZP SCF	509	554	447	415
DZP MP2	481	531	404	376

of theory the D_{2h} chemically bound global minimum (3) is found to lie 198 kcal/mol below 1 and 35 kcal/mol below 2.

The high-energy content of these N₈ isomers suggests that they may be useful as explosives or propellants, as noted in previous studies of the O_h structure (1).^{7,8,10} An effective propellant is characterized by a high ratio of energy release to mass and by a high specific impulse, *I_{sp}*.³² To estimate these quantities we consider the unimolecular reaction N₈ → 4N₂, as has been done in previous studies of octaazacubane (1).^{7,8,10} Although a detailed analysis of this reaction is beyond the scope of the present study, we note that the symmetry rules for the decomposition of 1 and 2 are identical to those for the analogues cubane and cyclooctatetraene, both of which are well-known experimentally. For the planar structure 3, dissociation to 4N₂ would seem to require breaking the bond between the two bridging nitrogens. Given this, conceptually the simplest dissociation mechanism involves breaking every other bond along the perimeter, so that the reaction coordinate preserves at most C_{2h} symmetry. A comparison of orbital occupancies for the reactants and products indicates that this process is symmetry-forbidden for a reaction coordinate preserving C_{2h} symmetry, but it becomes symmetry-allowed under C₂ symmetry; this suggests that the dissociation N₈ (3) → 4N₂ may involve a ring puckering.

The energy release to mass ratios and *I_{sp}* estimates are presented in Tables 5 and 6 and are compared with values for other HEDM candidates. At the MP2 level of theory the nitrogen compounds give dissociation energies (per mole of atoms) which are 2–3 times greater than those of the oxygen HEDMs. Following Engelke,⁸ we use a 4.7:1 by weight mixture of O₂ to H₂ as a comparison propellant; the estimated value for the *I_{sp}* of this mixture is 456 s. We see that both O_h N₈ (1) and I_h N₂₀ outperform the standard oxygen/hydrogen mixture as propellants, while D_{2d} N₈ (2) and D_{2h} N₈ (3) perform somewhat worse than the standard, according to the *I_{sp}* estimates.

Although the cube structure is clearly the most energetic, at the present there seems no obvious synthetic route to octaazacubane (1), due to it being such a high-lying structure on the potential energy surface. However, 1 might be synthesized by going through other N₈ minima. For example, two photochemically allowed [2+2] cycloadditions will yield 1 starting from 2. The D_{2h} structure (3) appears to be the most realistic target for synthesis. Although this structure is not as energetic as the other two structures, it nevertheless lies 225 kcal/mol above four nitrogen molecules, making it a possible high energy density material.

Conclusions

We have reported theoretical geometries, energies, and harmonic vibrational frequencies for three isomers of N₈. Each

structure is found to be high-lying in energy with respect to $4N_2$, and each represents a minimum on the potential energy hypersurface at the DZP SCF and DZP MP2 levels of theory. Due to their high energy content, these metastable structures may be useful as explosives or propellants. Simple estimates of the specific impulse (I_{sp}) for these structures give favorable results, particularly for octaazacubane (**1**). Of the three minima characterized, the planar bicyclic structure (**3**) appears to be the easiest synthetic target, while boat structure (**2**) may be a useful intermediate in the synthesis of **1**. Structure **3** is particularly interesting as a possible metastable all-nitrogen aromatic compound.

Acknowledgment. The authors would like to thank Ben Gimarc for helpful comments concerning pentalene and the D_{2h} bicyclic structure (**3**) and for suggesting the boatlike D_{2d} structure (**2**) and the Lewis structure (Figure 4); Peter Schreiner for helpful discussions and for suggesting structure **3**; Horst Sulzbach for advice on MP2 and CADPAC; Roger Grev for his helpful insights into group theory; and Craig Marsh for his help with the vibrational analysis. This material is based upon work supported under a National Science Foundation Graduate Fellowship to C.D.S. This research was supported by the U.S. Air Force Office of Scientific Research Grant AFOSR-92-J-0047.

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JP942408M